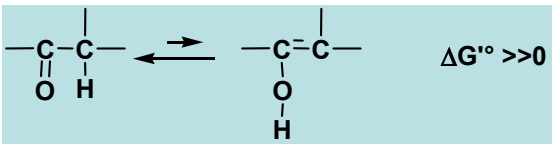
# Ketoenolic tautomery

## Ketoenolic tautomeries



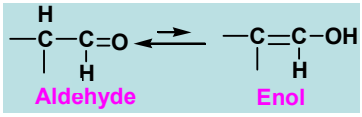

- Ketoenolic tautomeries are always endergonic when the enol is formed. Inversely, the return to aldehyde or ketone liberates energy.

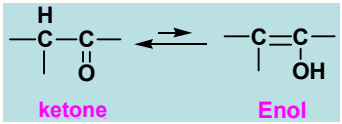
- Therefore, Ketoenolic tautomeries are reactions coupled to themselves (double ketoenolic tauotomery) or to other reactions.

Double ketoenolic tauotomery are reactions that allow the transposition and isomerization of sugars. In the case of isomerization the reaction is reversible.

# Ketoenolic tautomery

- **Substrates: these reactions take place in substrates having a C-H in position α of an aldehyde or a ketone.**

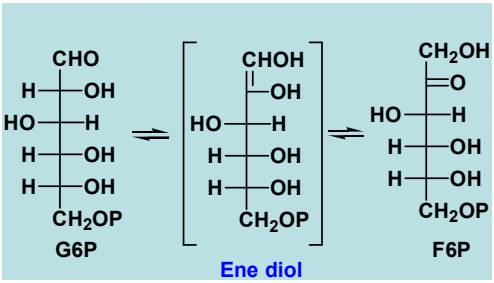



**endergonic reactions (ΔG'°>>0), so they are directed to left.**

**Ketoenolic tautomery reactions are very quick, they occur in the enzyme active site catalyzing the associated coupled reaction.**

**Mechanism of transposition of sugars or P-sugars (ex ; G6P⇆ F6P)**




**Fixation of G6P on the isomerase stabilize the enediol, this allows the transposition**

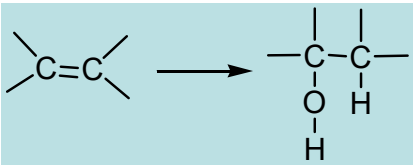
# Hydration
# Dehydration

**Hydration and dehydration reactions are all reversible ($\Delta G'^{\circ}=0$)**

**However, a polarizing effect is required and most often obtained by previously synthetizing coenzyme A condensates.**

## Hydration Dehydration

- Hydration involves the addition of a entire $H_2O$ molecule into a double bond : in general carbon = carbon.




- The C=C function must be at the vicinity of an electron attractor function. If the polarization is not sufficient, an activator coenzyme (most times HSCoA) is fixed into the vicinity of a C-C that will then be transformed into the C=C to be hydrated (see Lynen catabolism).

- Hydration and dehydration reactions are always reversible.

# Conclusion : Types of reactions

Transformations of aliphatic compounds in the metabolic pathways always involve one or several of the simple reactions on one of the 5 categories:
(The transformation of aromatic compounds is more complex).

Major processes :

- Oxidation / reduction
- Hydrolysis / condensation
- C-skeleton synthesis / C-skeleton breakdown

Minor processes:

- Ketoenolic tautomery
- Hydration / dehydration

*In the examination you will identify the reaction(s).*

The sub-types (isomerization, decarboxylation…) will be considered only if the type of reaction is correctly mentioned.

For coupled reactions, you will have to mention all of them
(for ex. Oxidation + condensation)

Exemples : Glycolysis and fatty acid catabolism (Lynen catabolism) involve the 5 types of reactions :

"Hydrolyse - Condensation ": action of a ligase and a thiolase (coupled reactions)

- Hydrolysis is exergonic and condensation is endergonic.
- Condensation is often coupled with a hydrolysis, while C-C bond breakdown is coupled with an oxidation.

"C-C bond breakdown " :

With few exceptions, C-C bond synthesis and breakdown are not red-ox : the reduction corresponding to C-C bond breakdown is compensated by an oxidation.

"Oxido-reduction" : action of dehydrogenases $NAD^+$ or FAD dependent

- FAD allows oxidation of alkyl groups (function degrees=0). It requires an activated/mobile H in the vicinity of the reactive C-H.
- $NAD^+$ allows oxidation of functions with function degrees = or > 1.

"Hydration" : action of dehydratase

- Hydration - dehydration reactions are reversible ($\Delta G'^\circ=0$)

Ketoenolic tautomery

- Ketoenolic tautomery reactions are endergonic in the directions of enol formation ($\Delta G'^\circ>0$).
- Thus, these reactions are always coupled to other reaction, many times the inverse ketoenolic tautomery (sugar transposition by double Ketoenolic tautomery) or others (degradation of PEP).